

# Thermodynamics of precipitation from mixed micellar solutions

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## Abstract

The equilibrium of the precipitate with mixed micellar solutions of the following types, (1) two ionic surfactants with the same hydrophobic chain but different counterions and (2) anionic + semipolar surfactants, are considered. Simple thermodynamic models that yield the composition dependence of the dissolution temperature in the ternary system (at fixed overall surfactant content) are discussed. The description is performed in terms of composition variables of aqueous pseudo phase (solubility product approach) or micellar pseudo phase. The latter approach has appeared efficient for prediction of solubility diagrams in concentrated ternary systems with the use of data for aqueous solutions of pure surfactants. Results of calculations are compared with experimentally studied solubility diagrams for mixed aqueous systems of (1) dodecylsulfates of sodium and magnesium and (2) sodium dodecylsulfate + dodecylamine oxide. The mixtures are studied at overall surfactant contents significantly higher than the CMC. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Model; Data; Solid–liquid equilibrium; Ternary mixtures; Ionic surfactants

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## 1. Introduction

Surfactant precipitation from aqueous solutions is of practical importance in detergency, petroleum production, surfactant separation processes, etc. In some cases (e.g., detergency) precipitation can be deleterious and it is desirable to extend the concentration range of unsaturated solutions and decrease the precipitation temperature by adding other substances to the surfactant solution. On the other hand, precipitation can help in recovery of surfactants from mixtures used in surfactant-based separation processes and in the process of surfactant-enhanced water-flooding of oil reservoirs. Precipitation behavior can be manipulated to a great extent when one deals not with a single surfactant system but with surfactant mixtures. Thus, understanding precipitation phenomena in mixed surfactant systems is

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a problem of great actuality in practical applications. Evidently, it also has a fundamental scientific significance, among other problems of physical chemistry of aggregated fluid systems.

Two types of precipitation data for mixed micellar systems are published in the literature: (1) phase boundaries (the concentration of an additive vs. the surfactant concentration for saturated solutions) at constant temperature and (2) precipitation (dissolution) temperatures (the Krafft temperatures) vs. concentration. In the latter case, some composition variable (for example, total surfactant concentration) is fixed. The dependence of temperature on surfactant-based mole fraction is usually considered for aqueous mixtures of two surfactants. Primary attention has been paid to precipitation of anionic surfactants at isothermal conditions [1–13]. The hardness tolerance of the anionic surfactant (the minimum concentration of multivalent cations necessary to cause precipitation of the surfactant) and salinity tolerance (the minimum concentration of monovalent cations causing precipitation) in single anionic surfactant (plus salt), anionic–nonionic, anionic–anionic and anionic–cationic surfactant mixtures have been studied. It is worth mentioning that solid phases crystallising from micellar solutions usually have constant composition (pure surfactant or its hydrate, some complex, ice); formation of solid solutions is observed only rarely [14]. The Krafft temperature vs. surfactant-based mole fraction at fixed total surfactant content (0.01–0.15 mol/l) was measured for several mixtures of anionic surfactants [2,15,16]. Eutectic type diagrams having two branches, each corresponding to crystallization of one of the surfactants, were observed. Also, two branches were observed in curves of the dependence of precipitation temperature on the concentration of multivalent salts added to a solution of sodium dodecyl- or ethoxydodecylsulfate [17]. It was found that temperature vs. relative surfactant concentration curves for mixtures of anionic and cationic or zwitterionic surfactants have two eutectics and a temperature maximum between them [15,18]. The occurrence of the temperature maximum permitted the researchers to conclude that the two surfactant species form complexes. In addition, there are measurements of the Krafft temperature aimed at the study of complex formation between quaternary cationic ammonium surfactants and various aromatic additives [19]. The effect of light amphiphilic additives on the dissolution temperature of nonionic surfactants in aqueous solutions has been discussed in our previous communications [20,21], where experimental data spanning a wide range of surfactant (*N*-dodecanoyl-*N*-methylglucamine) and additive (alkanol) concentrations and results of model calculations were presented. Experimental data and results of modeling of micellar solution–solid phase equilibrium for ternary systems containing two nonionic surfactant homologues have been presented in Ref. [22].

The pseudo-phase separation approach [23] has appeared helpful in the thermodynamic description of solubility diagrams in mixed nonionic [20–22,24] and ionic [3–12] surfactant systems. For the latter, the conditions of equilibrium between the micellar solution and the solid surfactant are formulated through the ions solubility product. Regular solution theory with one adjustable parameter is used, as a rule, to account for nonideality of mixed micelles, and the Debye–Huckel approximation is employed for the estimation of the activity coefficients of ions in the aqueous medium. Partial counterion binding at the micellar surface needs special consideration.

The objective of the present study is to model two types of surfactant aqueous systems, viz., (1) mixtures of anionic surfactants with the same hydrophobic chain but different in counterions (sodium and magnesium dodecylsulfates, henceforth abbreviated as SDS and  $\text{Mg}(\text{DS})_2$ ); (2) a semipolar + anionic system (dodecylamine oxide + SDS). Modeling was aimed at describing the dependence of the precipitation temperature on composition over a wide range of surfactant concentrations. In case (2), the pH effect on the solubility diagrams is also of interest.

## 2. Mixtures of dodecylsulfates of mono- and bivalent metals

Data on dissolution curves in systems of this type are limited [16], although many studies have been carried out for solutions of SDS with added salts of bivalent metals [6–12,17]. These solutions can be considered as containing two surfactants with the added salt. For example, SDS solutions with added  $\text{MgX}_2$  ( $X = \text{Cl}, \text{NO}_3$ , etc.) in the range of concentrations  $C_{\text{SDS}} > 0.5 \cdot C_{\text{MgX}_2}$  are equivalent to SDS +  $\text{Mg}(\text{DS})_2$  mixtures with added NaX. It is of interest to try how the models developed earlier for systems containing salt [2,6,7] will work in the case of analogous mixtures without any added salts and whether predictive modeling of micellar solution–solid phase equilibrium over a wide range of surfactant concentrations can be achieved. Special attention will be focused on rather concentrated micellar solutions, whereas literature data on solubility diagrams and model calculations usually relate to surfactant concentrations insignificantly above the CMC. A noticeable change of temperature along the Krafft boundary in binary SDS– $\text{H}_2\text{O}$  system gives evidence of a substantial increase in the activity of SDS with its growing concentration. To model these changes, a proper account of true concentrations of various ionic species and inter-particle interactions is needed which is a complicated task even for rather low surfactant concentrations [25]. At the same time, it seems that the effect of non-ideality should not be so pronounced for mixed solutions where the total surfactant content is fixed and the dependence of the dissolution temperature on relative concentrations of counter-ions is concerned.

As an example, we will discuss below the solubility diagrams for the sodium–magnesium dodecylsulfate system studied in our laboratory (Fig. 1). In Fig. 1 and below the surfactant-based mole fraction of component  $i$  is defined as:

$$x_i = \tilde{C}_i / (\tilde{C}_1 + \tilde{C}_2) \quad i = 1, 2,$$

where  $\tilde{C}_i$  is the molar concentration of SDS ( $i = 1$ ) or  $\text{Mg}_{1/2}$  ( $i = 2$ ). Solubility diagrams  $T(x_1)$  in Fig. 1 relate to the total molar content of the surfactants ( $C_{\text{surf}} = \tilde{C}_1 + \tilde{C}_2$ ) equal to 0.2 and 0.4 mol/l. As is seen, each of the diagrams has two branches, one corresponding to crystallisation of SDS, and the other,  $\text{Mg}_{1/2}\text{DS}$  (in fact hydrates are crystallised). Some shift of the curves with a change of  $C_{\text{surf}}$  is observed, but the slope of the curves remains practically the same. Along the line of crystallisation of component  $i$  it holds:

$$(\partial T / \partial x_i)_{C_{\text{surf}}} = (RT^2 / \Delta H_i) (\partial \ln a_i / \partial x_i)_{T, p, C_{\text{surf}}},$$

where  $\Delta H_i$  is the differential molar enthalpy of dissolution of component  $i$ ;  $a_i$  is its activity. Thus, one can conclude that the derivatives  $\partial \ln a_i / \partial x_i$  for the two values of  $C_{\text{surf}}$  under study are quite similar (though activities themselves differ in magnitude). It might mean that variation of relative concentration of two surfactants at  $C_{\text{surf}} = \text{const}$  does not cause significant changes in ionic activity coefficients.

In the frame of the pseudo phase separation model the conditions of the micellar solution–solid phase equilibrium can be written in terms of composition variables either of aqueous or micellar phases. The preference depends upon the type of the surfactant system. In case of mixed solutions of non-ionic surfactants the pseudo phase description can be conveniently carried out in terms of the micellar phase composition especially when gross surfactant concentrations surpass the CMC

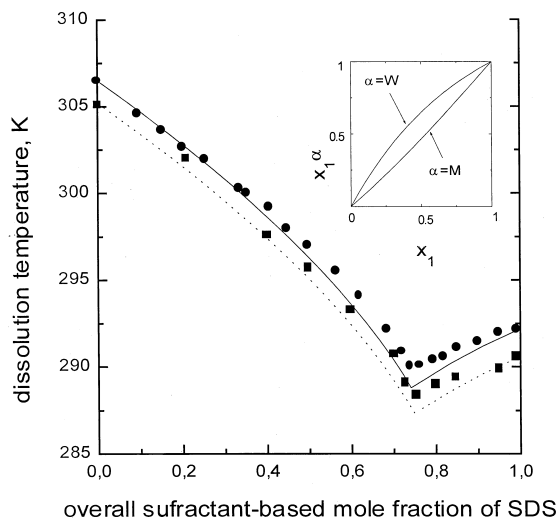


Fig. 1. The dissolution curves in the aqueous system SDS + Mg(DS)<sub>2</sub>. Points: experimental data, lines: description using solubility product approach:  $C_{\text{surf}} = 0.2$  mol/l (squares and dotted lines) and 0.4 mol/l (circles and solid lines);  $\Delta H_1 = 35$  kJ/mol,  $\Delta H_2 = 77$  kJ/mol,  $\beta_1^0 = \beta_2^0 = 0.8$ ,  $S = 4.25$ . Inset: The dependencies of the ion-based fractions of sodium ions,  $x_1^\alpha$ , in aqueous ( $\alpha = W$ ) and micellar ( $\alpha = M$ ) phases on the overall surfactant-based mole fraction of SDS in saturated solutions ( $C_{\text{surf}} = 0.4$  mol/l).

essentially [20,21]. Usually composition variables relating to the aqueous pseudo phase are employed when one deals with ionic surfactants [2,6–9]; precipitation condition is formulated as attaining the solubility product of ions in this phase. In aqueous solutions of SDS(1) and Mg(DS)<sub>2</sub>(2) the solubility product of surfactant  $i$ ,  $K_{si(a)}$ , is defined by the following expression:

$$K_{si(a)} = a_i a_{\text{DS}^-}^{n_i} = \gamma_i \gamma_{\text{DS}^-}^{n_i} C_i [\text{DS}^-]^{n_i} \quad (1)$$

where  $C_1$  and  $C_2$  are concentrations of ions Na<sup>+</sup> and Mg<sup>2+</sup> (mol/l) unbound by micelles, [DS<sup>-</sup>]<sub>—</sub>concentration of ions DS<sup>-</sup> which are not incorporated into micelles,  $n_i$ —electrovalency of ion  $i$ ;  $a_i$ ,  $a_{\text{DS}^-}$ ,  $\gamma_i$ ,  $\gamma_{\text{DS}^-}$ —activities and activity coefficients of corresponding ions. Activity of water is only slightly dependent on the micellar solution composition, and therefore expression (1) for the solubility product can be applied even in case when the solid phase is crystal hydrate. The dependency of  $K_{si(a)}$  on temperature is given by thermodynamic relation:

$$\ln K_{si(a)}(T) = \ln K_{si(a)}(T_i^0) - \frac{\Delta H_i}{R} \left[ \frac{1}{T} - \frac{1}{T_i^0} \right] \quad (2)$$

Here  $T_i^0$  is the dissolution temperature of the pure component  $i$  (SDS or Mg(DS)<sub>2</sub>) at a given value of  $C_{\text{surf}}$ ; the differential molar enthalpy of dissolution  $\Delta H_i$  relates to the transition of component  $i$  from the solid state to the dissociated form in aqueous solution. As mentioned above, at  $C_{\text{surf}} = \text{const}$  ionic activity coefficients vary with  $x_i$  only insignificantly. Thus, one can use the solubility product given in concentrations:

$$K_{si} = C_i [\text{DS}^-]^{n_i} \quad (3)$$

Combining Eqs. (2) and (3), one has the following relationship for the concentrations of unbound ions  $i$  in the solution saturated with surfactant  $i$  at temperature  $T$ :

$$\ln C_i(T) = \ln C_i(T_i^0) - \frac{\Delta H_i}{R} \left( \frac{1}{T} - \frac{1}{T_i^0} \right) + n_i \ln \frac{[\text{DS}^-(x_i = 1)]}{[\text{DS}^-(x_i)]} \quad (4)$$

Material balance constraints hold for the both counter-ion species:

$$C_{\text{surf}} x_i = n_i C_i + \beta_i (C_{\text{surf}} - [\text{DS}^-]), \quad (5)$$

here  $\beta_i$  is the binding degree of ion  $i$  by micelles (the fraction of aggregated  $\text{DS}^-$ -ions, whose charge is neutralised by counter-ion  $i$ ). In the range of concentrations far above the CMC the term  $[\text{DS}^-]$  in Eq. (5) can be neglected. Concentrations of unbound cations obey also the ion-exchange equilibrium condition which can be formulated theoretically with regard to the micellar surface potential [26]. The following simplified form was used in Ref. [7]:

$$S = \frac{\beta_2 C_1}{\beta_1 C_2}. \quad (6)$$

To estimate the temperature of crystallisation of surfactant  $i$  from ternary solutions one can use the binary data on  $T_i^0$  (at a given value of  $C_{\text{surf}}$ ),  $\beta_i^0$ , the binding degree of ion  $i$  in the aqueous solution of pure surfactant  $i$ , and  $\Delta H_i$  (the latter may be considered as independent of concentration). However, one should formulate how the concentration of non-aggregated  $\text{DS}^-$  ions and degrees of counter-ion binding  $\beta_i$  depend on  $x_i$ . There is much uncertainty about that. For diluted micellar solutions the assumption that  $\text{DS}^-$  concentration in a surfactant mixture is equal to the CMC at a given value of  $x_i$  is often used. This approximation is not valid for concentrated solutions. Observations by  $\text{DS}^-$ -selective membrane electrode carried out in our laboratory have shown that with growing surfactant concentration in micellar solutions the activity of  $\text{DS}^-$  decreases in case of SDS solutions more drastically than in solutions of  $\text{Mg}(\text{DS})_2$ . The measured values of  $\text{DS}^-$  activity at  $C_{\text{surf}} = 0.2$  and  $0.4$  mol/l in solutions of  $\text{Mg}(\text{DS})_2$  are even somewhat higher than in solutions of SDS. There are no experimental or theoretical data on the activities of ions ( $\text{DS}^-$  and cations) in mixed solutions at relatively high surfactant concentrations.

Our task was to examine the effect of various factors on the calculated results and to propose a practical approach to prediction of dissolution curves. In the calculations, the following binary data were used. Temperatures of precipitation from solutions of the pure surfactants at  $C_{\text{surf}} = 0.2$  and  $0.4$  mol/l are:  $T_1^0 = 290.6$  and  $292.2$  K for SDS and  $T_2^0 = 305.6$  and  $306.2$  K for  $\text{Mg}(\text{DS})_2$ . The dissolution enthalpies are:  $35$  kJ/mol for SDS [27,28] and  $\Delta H_2 = 77$  kJ/mol for  $\text{Mg}(\text{DS})_2$  [6].

The degree of counter-ion binding for pure solutions of SDS given in the literature spans the interval  $0.7$ – $0.9$ . Mostly in our calculations, we have set  $\beta_1^0 = 0.85$  or  $0.8$ . The binding degree  $\beta_2^0$  (for the solution of pure  $\text{Mg}(\text{DS})_2$ ) should not be less than  $\beta_1^0$ . However unambiguous data on it are unavailable, and so we either made a supposition  $\beta_1^0 = \beta_2^0$  or treated  $\beta_2^0$  as an adjustable variable. It was supposed that for the total binding degree of micelles it holds:

$$\beta_1 + \beta_2 = \beta_1^0 x_1 + \beta_2^0 (1 - x_1).$$

In most cases calculations were performed using approximation (6), the parameter  $S$  was adjusted. Some results were obtained with the use of another, more common, condition of ion-exchange equilibrium:

$$S = \frac{\beta_2^{1/2}}{\beta_1} \frac{C_1}{C_2^{1/2}} \quad (7)$$

The total number of adjustable parameters was either one ( $S$ ) or two ( $S$  and  $\beta_2^0$ ). The fit routine dealt with the dissolution curves pertaining to the surfactant concentration  $C_{\text{surf}} = 0.4$  mol/l, the data referring to the concentration 0.2 mol/l were predicted using the fit values.

The results obtained can be summarised as follows. Let us view first the approximation applied widely to dilute micellar surfactant mixtures:

$$[\text{DS}^-(x_i = 1)]/[\text{DS}^-(x_i)] \cong \text{CMC}_i/\text{CMC} \cong x_i + (1 - x_i)\text{CMC}_i/\text{CMC}_j \quad (j \neq 1), \quad (8)$$

where CMC stands for the critical micellar concentration (mol/l) in the aqueous surfactant mixture having the composition  $x_i$ , the quantity  $\text{CMC}_i$  relates to the aqueous solutions of pure component  $i$ . The approximation (8) gave satisfactory results only when unreasonably low values of  $\beta_2^0$  (about 0.5) were used. This result is not surprising because as mentioned above the relationship (8) is not obeyed for the studied range of concentration.

A satisfactory agreement with the experimental solubility diagrams (Fig. 1) was achieved in the approximations  $\beta_1^0 = \beta_2^0 = 0.85$  or 0.8 and  $[\text{DS}^-(x_1)] = \text{const}$  ( $1 \leq x_1 \leq 1$ ). The adjusted value of  $S$  (in Eq. (6)) was 4.11 or 4.25. The calculated dissolution curves were practically the same as in Fig. 1 in case of two fit parameters:  $\beta_2^0 = 0.83$ ,  $S = 3.7$  (with fixed value  $\beta_1^0 = 0.85$ ).

The experimental solubility curves could be reproduced satisfactorily (though a bit worse than in Fig. 1) in the supposition  $[\text{DS}^-(x_1 = 0)]/[\text{DS}^-(x_1 = 1)] \neq 1$  (the ratio was set 1.4 basing upon preliminary potentiometric measurements), the value of  $[\text{DS}^-]$  in mixtures being linearly dependent on  $x_1$ .

So, adjusting parameter  $S$  (and sometimes  $\beta_2^0$ ) one can describe the solubility curves in the ternary system under study using various versions of the dependence  $[\text{DS}^-](x_1)$  and various characteristics of the ion-exchange equilibrium. For predictive purposes the assumption  $(\text{DS}^-) = \text{const}$  with one adjustable parameter  $S$  seems the most useful, but the range of applicability of the approximation has to be examined. The calculations of concentrations of ions in the aqueous and micellar phases performed using solubility product formalism gave grounds for employing another, much more simplified, approach. It has been found that for all the versions tried (including ion-exchange equilibrium condition (7)) the relative concentrations of sodium and magnesium ions in micelles are very close to their overall ratio in the system. An example is given in the inset of Fig. 1, where quantities  $x_1^{\text{M}} = \beta_1/(\beta_1 + \beta_2)$ , ion-only-based fraction of sodium ions in micelles, and  $x_1^{\text{W}} = C_1/(C_1 + 2C_2)$ , the fraction in the aqueous phase, are plotted vs.  $x_1$ . The linearity of the reciprocals  $x_1^{\text{M}}$  vs.  $x_1$  is quite natural for solutions under study, where the gross surfactant concentration is rather high and the overall degree of counter-ion binding is close to unity. Thus, for concentrated mixtures of two anionic surfactants, it becomes convenient to describe the solid–liquid equilibrium using the composition variables of the micellar pseudo phase like in case of non-ionic surfactant mixtures [22].

Consider the surface of the micellar core (organized by  $\text{DS}^-$  anions and covered by counter-ions) as a two-component lattice system: monomer  $\text{Na}^+$ , dimer  $\text{Mg}^{2+}$  and vacancies. Let  $\varphi_i$  denote the

volume fraction of component  $i$  in such system. Owing to the aforementioned equality of the relative concentrations of counter-ions in the micellar phase and the entire system, one can write:

$$\varphi_1 = x_1 \quad \varphi_2 = x_2 \quad (9)$$

For the micellar pseudo phase in equilibrium with solid surfactant  $i$  it holds:

$$\ln a_i = -\frac{\Delta H_i}{R} \left[ \frac{1}{T} - \frac{1}{T_i^0} \right], \quad (10)$$

where  $a_i$  stands for the activity of surfactant component  $i$  in the micellar phase;  $a_i = 1$  at  $\varphi_i = 1$ . The meaning of the variable  $\Delta H_i$  is the differential enthalpy of transition of pure surfactant  $i$  from the solid state into the micellar solution. It differs from  $\Delta H_i$  in Eq. (2) for the enthalpy of micellization.

The activities in the micellar phase were described by the Flory equations for a monomer–dimer mixture:

$$\begin{aligned} \ln a_1 &= \ln \varphi_1 + \varphi_2/2 + \chi \varphi_2^2 \\ \ln a_2 &= \ln \varphi_2 - \varphi_1 + 2\chi \varphi_1^2, \end{aligned} \quad (11)$$

where  $\chi$  is the energy parameter.

Insofar as the enthalpy of micellization of SDS reported in the literature is small and changes its sign with temperature [28], the value 35 kJ/mol has been ascribed to  $\Delta H_1$  like in calculations basing on the solubility product concept. According to our calorimetric measurements, differential molar enthalpy of transition of  $\text{Mg}(\text{DS})_2$  from the solid state to the micellar solution is 100 kJ/mol. The results of calculations using Eqs. (10) and (11) are in a satisfactory agreement with the experiment, even if one assumes that  $\chi = 0$  (Figs. 2 and 3; in this case the calculations are based solely on the binary data, no parameters are adjusted). The dissolution curves obtained with the fit value of  $\chi$  ( $-0.023$ ) are very close to those at  $\chi = 0$ .

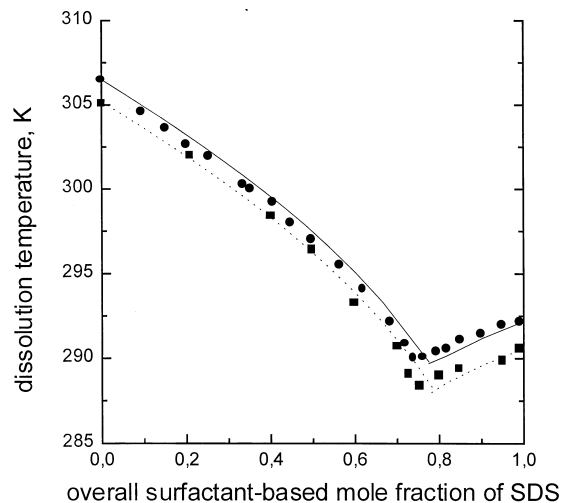


Fig. 2. The dissolution curves in the aqueous system SDS +  $\text{Mg}(\text{DS})_2$ . Points: experimental data, lines: description using Eqs. (10) and (11) with  $\chi = 0$  (no adjustable parameters).  $\Delta H_1 = 35$  kJ/mol,  $\Delta H_2 = 100$  kJ/mol.

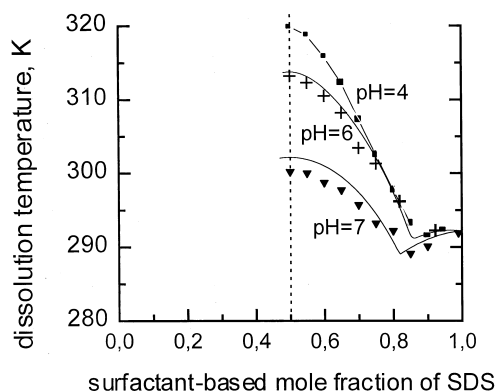
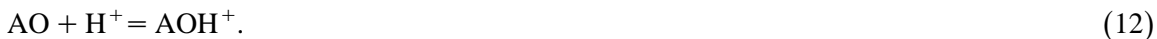


Fig. 3. The dissolution curves in the system AO-SDS (the overall weight content of the surfactants is 10% wt.) Points - experimental data, solid lines - thermodynamic description:  $T_1^0 = 292.2$  K,  $T_2^0 = 319.9$  K,  $\Delta H_1 = 35$  kJ/mol,  $\Delta H_2 = 34.7$  kJ/mol,  $K_a = 3 \times 10^{-5}$ ,  $K_{AOS} = 5.1 \times 10^2$ ,  $\beta_1^0 = 0.85$ .

To conclude, the solubility diagrams for mixtures of SDS and  $\text{Mg}(\text{DS})_2$  at their relatively high overall content can be predicted basing upon the binary data in the way similar to that for mixtures of non-ionic surfactants [22]. In this paper surfactant mixtures without added salt were considered. The description in terms of the composition variables of the micellar pseudo phase can be extended straightforwardly to mixtures of anionic surfactants containing salts. In this case conditions of ion-exchange equilibrium and effects of non-ideality should be taken into account.

### 3. Mixtures of anionic and semipolar surfactants

Aqueous solutions of SDS and alkylamine oxides (denoted as  $\text{C}_n\text{AO}$  or AO) are typical examples of the systems under discussion. The behavior of these mixtures has been paid much attention in literature [15,29–34]. It is strongly influenced by the process of amine oxide protonation:



Like in mixtures of anionic and cationic surfactants, ionic pairs are formed:



Strong synergistic effects (depending on pH) and a sophisticated topology of phase diagrams are peculiarities of the discussed systems. The Krafft temperature vs. composition diagrams for aqueous systems  $\text{SDS}-\text{C}_n\text{AO}$  ( $n = 12, 14$ ) at natural pH (about 8) indicated that an addition compound  $\text{DS}:\text{AO} = 1:3$  is formed [15]. According to the data recently obtained in our laboratory, the temperature maximum relating to the formation of a 1:1 complex occurs at lower pH. The value of the maximum temperature grows with growing acidity, which is the indication of growth of the concentration of the complex. However, on diminishing pH, starting from about 5 there was no change in the location of the experimentally observed dissolution curves. The effects of pH on the



solubility diagrams were not studied until now and our goal was to model these phenomena. The discussion below pertains to surfactant concentrations significantly above the CMC. In this region the composition of mixed micelles is approximately equal to the overall surfactant-only-based composition of the solution ( $x_i$ ,  $i = \text{AO, SDS}$ ). The *true* equilibrium composition of the micellar system is described by the variables  $z_i = \tilde{m}_i / (m_{\text{AO}} + m_{\text{SDS}})$ , where  $\tilde{m}_i$  ( $i = \text{AOS, DS}^-, \text{AO, AOH}^+$ ) are the overall numbers of moles of the various species, and  $m_{\text{AO}}$  and  $m_{\text{SDS}}$  are the overall numbers of moles of the surfactants.

*True* compositions can be found from the conditions of chemical equilibria:

$$K_a = \frac{z_{\text{AOH}^+}}{z_{\text{AO}} 10^{-\text{pH}}} \quad \text{and} \quad K_{\text{AOS}} = \frac{z_{\text{AOS}}}{z_{\text{DS}^-} z_{\text{AOH}^+}} \quad (14)$$

and the material balance constraints. Combining the latter with Eq. (14) gives:

$$z_{\text{AOS}}^2 - z_{\text{AOS}} \left[ 1 + \frac{1}{K_{\text{AOS}}} \left( 1 + \frac{1}{10^{-\text{pH}} K_a} \right) \right] + x_{\text{AO}} (1 - x_{\text{AO}}) = 0. \quad (15)$$

Knowing the values of  $K_a$  and  $K_{\text{AOS}}$  (which are assumed to be temperature-independent) one can find the *true* concentrations of the various species in the mixture of a given overall composition  $x_{\text{AO}}$ .

The solubility diagram is considered in the range of concentrations  $0.5 \leq x_{\text{SDS}} \leq 1$  (for higher content of AO, the complexes of stoichiometry other than 1:1 might be formed). For the branch of crystallization of SDS (component 1) the *true* concentrations of ions are substituted into Eq. (2), which gives:

$$\ln K_{s1}(T) - \ln K_{s1}(T_1^0) = \ln \left\{ \frac{x_{\text{DS}^-} z_{\text{SDS}} \left( 1 - \beta_1 \frac{x_{\text{DS}^-}}{z_{\text{SDS}}} \right)}{1 - \beta_1} \right\}. \quad (16)$$

The binding degree of sodium  $\beta_1$  is supposed to be temperature- and concentration-independent. The branch of crystallization of AOS (component 2) was treated in the following way. The temperature and enthalpy of transition of the pure complex AOS from the solid to aggregated state ( $T_2^0 = 319.9 \text{ K}$ ,  $\Delta H_2 = 34.7 \text{ kJ/mol}$ ) were estimated from the experimental solubility diagram at  $\text{pH} = 4$  using the following relationship:

$$\ln(2x_{\text{AO}}) = - \frac{\Delta H_2}{R} \left( \frac{1}{T} - \frac{1}{T_2^0} \right) \quad (17)$$

Concentrations of various species at higher pH were calculated from Eq. (10). For the protonation constant  $K_a$  a value of  $3 \times 10^{-5}$ , obtained from potentiometric titration experiments, was used (it agrees well with the value from Ref. [30]). The fit value  $K_{\text{AOS}} = 5.1 \times 10^2$  was obtained from the set of experimentally observed dissolution curves at various pH. It relates to a concentrated micellar system and, therefore, evidently differs from the constant of complex formation between monomeric species in the diluted aqueous solutions.

As seen in Fig. 2, the calculations reproduce general trends in the location of the solubility curves in the system  $C_{12}AO + SDS$  at various pH.

#### 4. Conclusion

Calculations performed for aqueous  $SDS-Mg(DS)_2$  solutions have shown the possibility to describe the solubility diagrams for rather concentrated surfactant mixtures employing the solubility product approach. The input information for prediction bases on the experimental data for aqueous solutions of pure surfactants, two or one model parameters are adjusted. The shortcoming of the description is in a need to make assumptions concerning dependence of the concentration of non-aggregated surfactant on the overall composition of the system. The composition of mixed micelles in concentrated surfactant mixtures (without added salts) has proved to be close to the overall surfactant-based composition. Because of this modeling of the precipitate–micellar solution equilibrium in terms of composition variables of the micellar pseudo phase has also been examined. This approach appeared to be efficient like earlier in case of non-ionic surfactants. Satisfactory agreement with the experimental results in mixtures of the two anionic surfactants under study has been achieved using only binary data (without adjusting of parameters or making any guesses concerning equilibrium concentration of ionic species in the aqueous phase).

The pH effect on the solubility diagrams of semipolar-anionic surfactant mixtures, not studied previously, was satisfactorily reproduced for the  $SDS-C_{12}AO$  system by the proposed version of the pseudo-phase model considering the reactions of protonation and complex formation. Assuming formation of a 1:1 complex, one can describe the solubility diagram in the range of mixing ratios  $SDS:C_{12}AO$  from 1:0 to 1:1. As for mixtures enriched with amine oxide where non-equimolar complexes can be formed, further experimental and theoretical studies would be of interest.

#### 5. List of symbols

$C_i$	Concentration of unbound cations $i$ , mol/l, ( $i = 1$ for $Na^+$ and $i = 2$ for $Mg^{2+}$ )
$\tilde{C}_i$	Concentration, mole/l, of $SDS$ ( $i = 1$ ) or $Mg_{1/2} DS$ ( $i = 2$ )
CMC	Critical micellar concentration (mol/l) of mixed surfactant
$CMC_i$	Critical micellar concentration (mol/l) in the aqueous solution of pure surfactant $i$
$C_{surf}$	Overall surfactant concentration (mol/l)
$\Delta H_i$	Differential molar enthalpy of dissolution of surfactant $i$ (J/mol)
$K_a$	Protonation constant of amine oxide
$K_{AOS}$	Stability constant of the complex between $AOH^+$ and $DS^-$
$K_{si}$	Solubility product of ionic surfactant $i$
$\tilde{m}_i$	Number of moles of species $i$ in solution of $AO$ and $SDS$ ( $i = AOS, DS^-, AO, AOH^+$ )
$m_i$	Overall number of moles of surfactant $i$ ( $i = SDS, AO$ )
$n_i$	Charge of cation $i$
$R$	Gas constant
$S$	Constant of ion-exchange equilibrium between the aqueous and micellar pseudophases
$T$	Temperature

$T_i^0$	Dissolution temperature of pure component $i$ at $C_{\text{surf}}$
$x_i$	Surfactant-based mole fraction of component $i$ ( $i = \text{SDS, Mg}_{1/2}\text{DS, AO}$ )
$x_i^\alpha$	Relative fraction of $\text{Na}^+$ ( $i = 1$ ) or $1/2 \text{Mg}^{2+}$ in the micellar ( $\alpha = \text{M}$ ) or aqueous ( $\alpha = \text{W}$ ) phase
$z_i$	Mole fraction of component $i$ in the mixture of AOS, $\text{DS}^-$ , AO, $\text{AOH}^+$
<i>Greek</i>	
$\beta_i$	Fraction of $\text{DS}^-$ ions in micelles, whose charge is compensated by counter-ions of sort $i$

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